Towards the "soft-landing" adsorption of doped Helium nanodroplets: key role of the He-TiO_2(110) interaction

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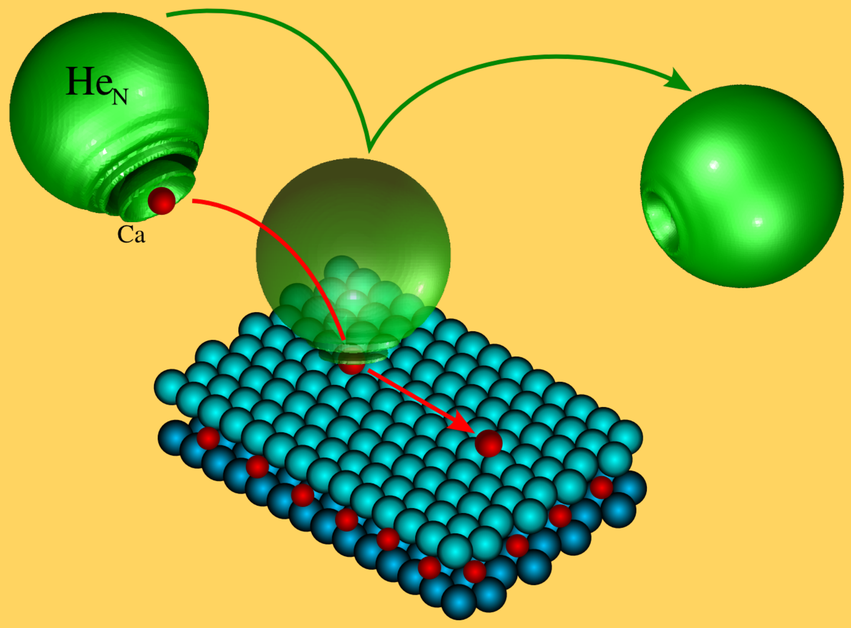
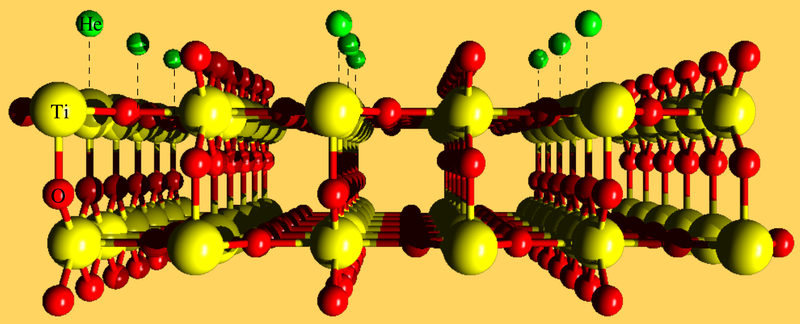
Introduction

Modification of surfaces to control their chemical and physical properties is of interest in many areas of science, including microelectronics, catalysis, optics and electrochemistry. Usual techniques include: 1) ion implantation using high energy ion beams (~1000 eV); 2) collisions of hyperthermal energy (~100eV) gas-phase ions; and 3) soft-landing of polyatomic ions using low energy beams (~10 eV), allowing their "intact" deposition[1]. Recently, a novel controlled deposition "soft-landing" technique has been proposed through the embedding of the targeted molecule in helium nanodroplets (collision energies ~0.1eV). Since the helium nanodroplet adsorbs the excess collision energy, this technique allows the sticking of a dopant-substrate physisorption state, both the dopant and the surface remaining intact (e.g., it avoids a charge transfer process between them that could lead to the dissociation of the former).





$TiO_2(110)\cdots He$

Objective

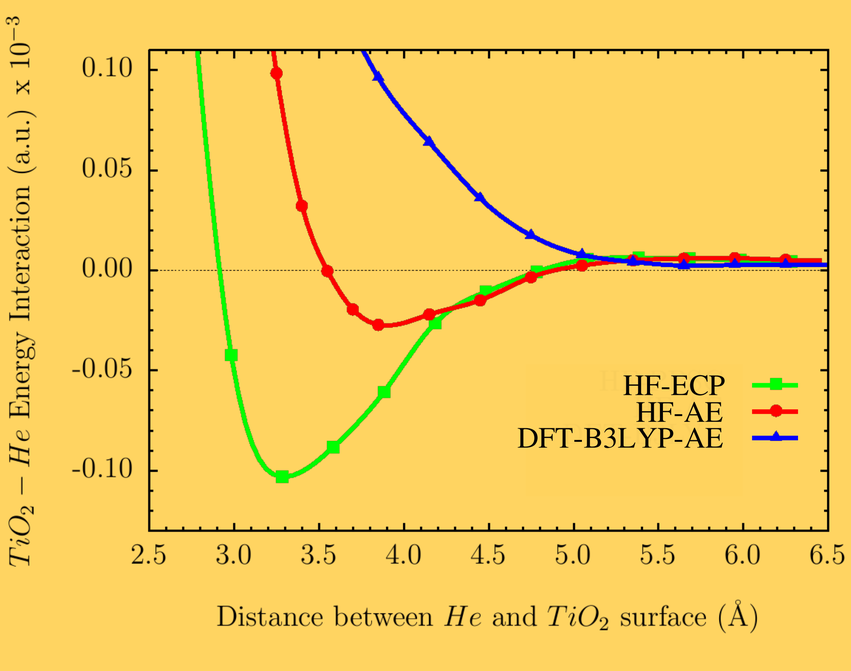
Our project addresses the computational simulation of the "soft-landing" of atomic and molecular impurities attached/embedded to/on helium nanodroplets (He_N, $N \leq 1000$) on a TiO_2(110) surface. In order to describe the interaction potentials we have appealed to the pair-wise approximation for dopant-He, He-surface and dopant-surface interactions, and quantum-chemistry-like treatments to model the He_N-dopant system[3,4]. Since the He-surface and the dopant-surface interactions are mainly dispersive and/or electrostatic (e.g., the He-surface physisorption well depth is typically of about 10 meV[2]), an extremely high precision is required to obtain reliable potential energy surfaces (e.g., including correlation at Møller-Plesset and Coupled-Cluster levels of theory).

Geometry Optimization

The calculations were performed using CRYSTAL code[5]. We have used for the electron calculations TVAE**, TVAE* and aug-cc-pVTZ electronic basis set for the Ti, O and He atoms, respectively, Hay-Wadt small core for Ti and Duran-Barthelat Electron Core Pseudopotentials(ECP) for O, were employed; with the same electronic basis set for the He atom in ECP calculations. The optimization of the slab molecular structure has been carried out through the default methods available in CRYSTAL.

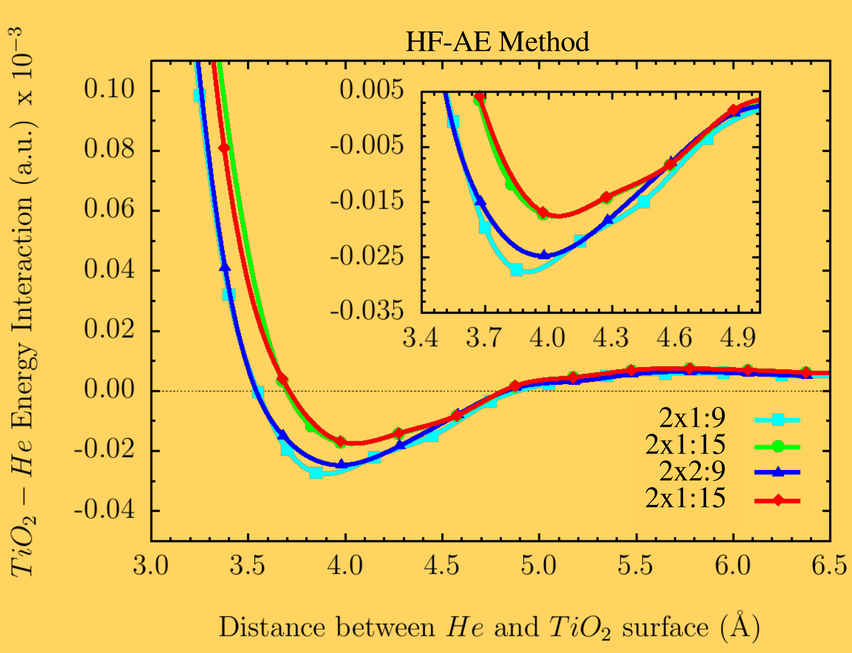
The tetragonal unit cell of the rutile TiO_2(110) contains two Ti and four O atoms, and is characterized by the lattice parameters a and c. As shown in the table the results agree well with the experimental data for the three methods, several number of layers and supercell dimentions, but the best result is for HF all electron calculations.

Method	Supercell dimensions	a(Å) exp. 2.959	b(Å) exp. 6.497
HF, All electron			
	2x1:9	2.955	6.503
	2x2:9	2.955	6.503
	2x1:15	2.969	6.474
	2x2:15	2.969	6.474
HF, ECP			
	2x1:9	2.999	6.381
	2x2:9	2.999	6.381
	2x1:15	3.007	6.368
	2x2:15	3.007	6.368
DFT-B3LYP, All electron			
	2x1:9	2.958	6.574
	2x2:9	2.981	6.548
	2x1:15	2.972	6.545
	2x2:15	2.971	6.549



Potential Energy Curves

We calculate the interaction energy between the slab and the He atom changing their realtive distance but keeping fixed the geometry of the slab. The Boys-Bernardi counterpoise scheme is used. The results show that the well depth is very sensitive to the employed method. In the specific case of the HF all electron calculation, the variation of the interaction energy with the number of layers in the slab is large, while it is small as a function of the supercell size.



Work in Progress

In order to describe the dispersive part of the He and molecule surface interactions, more sophisticated descriptions are required, including a proper treatment of the dynamical electronic correlation. To this end, we plan to perform (periodic) Möller-Plesset second order (MP2) perturbation theory by using the CRYSCOR module from the CRYSTAL code.

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